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The objective of this research was the characterization of molecular species which are important because of (a) their occurrence in high-temperature environments, as for example in the vapor over refractory solids, and in combustion, flames, and propellant burning; (b) their relevance to clarification and/or extension of the basic theory of molecular properties. The molecules studied were usually highly reactive or metastable and often inaccessible by the usual gas-phase spectroscopic methods. They were therefore trapped in a solid next page

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cont. matrix, usually neon or orgon, at $4^\circ K$ and investigated by optical and electron-spin-resonance (ESR) spectroscopies. This isolation procedure is known to produce only small perturbations and to yield information pertinent to the gas-phase species. The species studied included boron and bromine atoms, methylene radicals, diatomic boron, beryllium hydroxide, diatomic chlorine anion, carbonyl silene, diazasilene, the first-row transition-metal mono-, di-, and tri-fluorides and their corresponding hydrides and oxides, and a few rare-earth hydrides and fluorides. Vibrational frequencies, electronic transitions, g factors, spin-rotation constants, hyperfine coupling constants, zero-field-splittings, ground-state multiplicities, and perhaps some information about structure, were obtained. The molecules contained from one to seven unpaired electrons.

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8. PUBLICATIONS:

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9. RESEARCH OBJECTIVES

1. Characterization of molecular species which are important because of

   (a) their occurrence in high-temperature environments, as for example in the vapor over refractory solids, and in combustion, flames, and propellant burning.

   (b) their relevance to clarification and/or extension of the basic theory of molecular properties.

Such species are usually highly reactive and often inaccessible for study by the usual gas phase methods.

2. Exploitation of the matrix-isolation technique to allow the experimental investigation of molecules that are presently impossible or very difficult to study spectroscopically in the gas phase, particularly via electron-spin-resonance (ESR). In this technique the vapor species are trapped in solid neon or argon on a transparent window or dielectric surface at $4^{o}K$. The essential virtues of this procedure are (i) the long lifetime of the metastable species in such an inert rigid environment and at such a low temperature, and (ii) the population of only the zero-point vibrational level of the ground electron state of the molecule at $4^{o}K$.

10. ACCOMPLISHMENTS

Optical and ESR spectroscopy, and theory, have been applied to characterize a wide variety of small molecules meeting the above criteria. Generally these are the hydride, fluoride, and oxide molecules of the transition and rare-earth metals (usually of high spin), but radicals such as CH_2, BeOH, B_2, and SiCO have also been studied. Abstracts of most of the papers dealing with these molecules are given on the next few pages.

B atoms, B_2 and H_2BO molecules: ESR and optical spectra at 4°K*

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(Received 3 March 197(6))

Elemental boron has been vaporized and trapped in solid argon at 4-10°K. The Douglas Herzberg transition of B_2 has been observed in absorption at 3300 Å at 10°K, indicating that the lower Σ state is the ground electronic state. However, B_2 was not observed via ESR, which is interpreted as support for a $^3\Sigma_g$ ground state with a zero-field splitting greater than about 4 cm^{-1}, rather than $^5\Sigma_u$ favored by *ab initio* calculations. The ESR spectrum of B atoms in solid argon is also detected. It exhibits axial symmetry and almost complete quenching of the orbital angular momentum of the $^2P_{1/2}$ free atom, with $g_{\parallel} = 2.0014(5)$, $g_{\perp} = 1.9645(30)$. The simple crystal field model has been applied in the interpretation of the g and hyperfine tensors and comparison made with Al and Ga in argon, as studied by Ammeter and Schlosnagle. The ESR spectrum of H_2BO, appearing as an impurity, was observed for the first time, and its magnetic parameters determined.

ESR of Cl_2^- in various ion pairs at 4 °K and the theory of *V* centers

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(Received 21 July 1976)

ESR spectra have been measured of $M^+Cl_2^-$ ion pairs trapped in solid argon at 4°K, where M = Mg, Ca, Sr, Ba, Li, Na, and K. The derived *g* and hyperfine tensors of Cl_2^- are interpreted using the simple crystal field model of Schoemaker, and the spin densities and crystal field parameters E_x are compared with those for *V* centers in alkali halide crystals. From matrix data, it is proposed that the isotropic hyperfine coupling parameter A_σ for interaction with ^{35}Cl in pseudo-"free" Cl_2^- be taken as 37 ± 1 G. A discussion is given pointing out an approximate linear correlation between the nearest interaction distance (*d*) and $\Delta g_\perp$ (or A_σ) among all the V_K centers. Constraints imposed by lattices of varying M^+/Cl^- radius ratios cause variations in *d* and in the s/p_z character in the antibonding Cl_2^- electron, leading to corresponding changes in A_σ and inverse changes in $\Delta g_\perp$. V_t centers, with minimum constraints, have maximum values of A_σ.

SiCO, SiN_2, and $Si(CO)_2$ Molecules: Electron Spin Resonance and Optical Spectra at 4 K

R. R. Lembke, R. F. Ferrante, and W. Weltner, Jr.*[1]

Contribution from the Department of Chemistry, University of Florida, Gainesville, Florida 32611. *Received August 2, 1976*

Abstract: The $^3\Sigma$ molecules carbonylsilene, SiCO, and diazasilene, SiNN, have been prepared by the vaporization and reaction of silicon atoms with N_2 or CO and trapped in various matrices at 4 K. Some or all sites in some matrices induced slight bending of the molecules. Isotopic substitution of ^{13}C, ^{18}O, ^{15}N, and ^{29}Si was employed to obtain hyperfine coupling data in the ESR and shifts in the optical spectra. In solid neon, assuming $g_\parallel = g_\perp = g_e$, D = 2.28 and 2.33 cm^{-1} for SiN_2 and SiCO, respectively. Hyperfine splittings confirm the CNDO calculated results which indicate that in both molecules the electron spins are largely in the $p\pi$ orbitals of Si. Optical transitions with vibrational progressions were observed beginning at 3680 and 3108 Å for SiN_2 and at 4156 Å for SiCO. IR spectra were obtained and stretching force constants calculated. An attempt was made to correlate these vibrational and electronic data with those for CCO and CNN. Annealing an argon matrix containing SiCO to 35 K led to the observation in the IR of $^1\Sigma$ $Si(CO)_2$, a silicon counterpart of carbon suboxide. A corresponding treatment of a SiN_2 matrix did not produce the N_2SiN_2 molecule, nor was the N_2SiCO molecule observed when both ligands were present.

TiF_2 and TiF_3 Molecules: Electron Spin Resonance Spectra in Rare-Gas Matrices at 4 K

T. C. DeVore and W. Weltner, Jr.*

Contribution from the Department of Chemistry, University of Florida, Gainesville, Florida 32611. *Received February 7, 1977*

Abstract: TiF_2 and TiF_3 molecules, produced by the vaporization of solid TiF_3 or a mixture of titanium and a solid fluoride, were trapped in neon and argon matrices at 4–10 K. ESR spectra indicated that TiF_3 has a trigonal axis of symmetry with $g_\perp$ = 1.8910 (2) and $g_\parallel$ = 1.9912 (2) and hyperfine tensor components $A_\parallel$(Ti) = −197.9 (2), $A_\perp$(Ti) = −178.2 (2), $|A_\parallel(F)|$ = 47.9 (2), and $|A_\perp(F)|$ = 11.5 (2) MHz (in solid neon). It was concluded that TiF_3 has a $^2A_1'$ ground state with the odd electron in a hybridized 4s and $3d_{z^2}$ Ti^{3+} orbital perpendicular to the planar (D_{3h}) molecule. The excited $^2E''$ state lies ~2000 cm^{-1} higher. The ESR spectrum of TiF_2 was that of a nonlinear triplet molecule. Its magnetic parameters are g_x = 1.9149 (2), g_y = 1.9229 (2), and g_z = 1.9880 (2), where the *z* axis is parallel to the F–F direction. The zero-field-splitting parameters are $|D|$ = 0.0782 (2) cm^{-1} and $|E|$ = 0.0021 (1) cm^{-1}. The lines were broad, and no hyperfine structure was resolved. Theoretical considerations indicate that the ground state is $^3B_1$ with the unpaired spins occupying essentially nonbonding d orbitals on titanium.

YbH and YbD molecules: ESR and optical spectroscopy in argon matrices at 4°K[a)]

Richard J. Van Zee, Mikell L. Seely, and W. Weltner, Jr.

Department of Chemistry, University of Florida, Gainesville, Florida 32611
(Received 3 March 1977)

YbH and YbD molecules have been prepared by the reaction of Yb and H(D) atoms during the formation of an argon matrix at 4°K. Yb atom and YbH absorption and emission spectra were observed. The magnetic parameters of YbH were determined from the ESR spectrum of the $^2\Sigma$ molecules (with Yb nuclear spin $I = 0$ and $I = 1/2$) to be $g_{\parallel} = 1.9953(4)$, $g_{\perp} = 1.9402(2)$, $A_{\parallel}(\mathrm{H}) = 226$ MHz, $A_{\perp}(\mathrm{H}) = 224$ MHz, $A_{\parallel}[^{171}\mathrm{Yb}\ (I = 1/2)] = 5266$ MHz, $A_{\perp}[^{171}\mathrm{Yb}\ (I = 1/2)] = 5724$ MHz. The hyperfine parameters indicate that the spin density is less than 20% on the hydrogen and that the bonding is largely $\mathrm{Yb^+H^-}$. By comparison of experimental parameters with calculated Yb and $\mathrm{Yb^+}$ data it is deduced that the unpaired electron occupies predominately the $6s\sigma$ orbital on $\mathrm{Yb^+}$ with smaller contributions of $6p\sigma$ ($\mathrm{Yb^+}$) and $1s\sigma$ ($\mathrm{H^-}$).

ESR spectra of the MnO, MnO_2, MnO_3, and MnO_4 molecules at 4°K[a)]

R. F. Ferrante, J. L. Wilkerson,[b)] W. R. M. Graham,[c)] and W. Weltner, Jr.

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(Received 15 August 1977)

The molecules MnO, MnO_2, MnO_3, and MnO_4 have been prepared by the vaporization and reaction of manganese atoms with O_2, N_2O, or O_3 and isolated in various inert-gas matrices at 4°K. ESR has been used to determine magnetic parameters which are interpreted in terms of molecular geometry and electronic structure. MnO is confirmed to have a $\sigma\pi^2\delta^2$, $^6\Sigma^+$ ground state with $g_{\perp} = 1.990(7)$ (assuming $g_{\parallel} = g_e$) and a zero-field splitting in accord with the gas phase value $D = 1.32\ \mathrm{cm^{-1}}$. Hyperfine splittings due to the $^{55}\mathrm{Mn}$ ($I = 5/2$) nucleus are $A_{\parallel} = 176(8)$ and $A_{\perp} = 440(11)$ MHz. MnO_2 is a linear $^4\Sigma^-$ molecule with probable configuration $\sigma\delta^2$, $|D| = 1.13\ \mathrm{cm^{-1}}$ (assuming $g_{\perp} = g_{\parallel} = 2.0023$), $A_{\perp} = 353(11)$, $A_{\parallel} = 731(11)$ MHz. MnO_3 exhibits very large hf splittings $A_{\perp} = 1772(3)$ and $A_{\parallel} = 1532(3)$ MHz indicative of a sd_{z^2} hybrid $^2A_1$ ground state of D_{3h} symmetry. The spectrum of MnO_4 is consistent with a C_{3v} molecule distorted from a $^2T_1$ electronic state in tetrahedral symmetry by a static Jahn–Teller effect. g and A tensors are slightly anisotropic: $g_{\parallel} = 2.0108(8)$, $g_{\perp} = 2.0097(8)$, $|A_{\parallel}| = 252(3)$, $|A_{\perp}| = 196(3)$ MHz. The electron hole is almost entirely in an oxygen π-bonded orbital with one oxygen atom displaced along its Mn–O bond axis.

Electron Spin Resonance of the Ytterbium Fluoride Molecule at 4 K

R. J. Van Zee, M. L. Seely, T. C. DeVore, and W. Weltner, Jr.*

Department of Chemistry, University of Florida, Gainesville, Florida 32611 *(Received August 4, 1977)*

Publication costs assisted by the Air Force Office of Scientific Research and the National Science Foundation

The electron spin resonance spectrum of the $\mathrm{YbF}(^2\Sigma^+)$ molecule matrix-isolated in solid argon has been observed at 4 K. **g** tensor and hyperfine tensor components have been measured: $g_{\perp} = 1.9954(5)$, $g_{\parallel} = 1.9975(5)$, $A_{\parallel}(\mathrm{F}) = 220(2)$ MHz, $A_{\perp}(\mathrm{F}) = 134(2)$ MHz, $A_{\parallel}[^{171}\mathrm{Yb}(I = 1/2)] = 7822(5)$ MHz, $A_{\perp}[^{171}\mathrm{Yb}(I = 1/2)] = 7513(5)$ MHz. The hyperfine splittings indicate that the spin density on fluorine is only about 2%, indicating that the molecule is essentially an ion pair, $\mathrm{Yb^+F^-}$. About 80% of the spin is in a $\mathrm{Yb^+}$ $6s\sigma$ orbital and the remainder in $5d\sigma$ and $6p\sigma$ on the metal ion. From $\Delta g_{\perp}$, the spin rotation constant is estimated to be $+0.0034\ \mathrm{cm^{-1}}$.

High spin molecules: ESR of MnF and MnF_2 at 4°K

T. C. DeVore,[a] R. J. Van Zee, and W. Weltner, Jr.[b]

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(Received 14 November 1977)

ESR spectra of the MnF and MnF_2 molecules trapped in neon and argon matrices have been observed at 4°K. MnF was found to have a $^7\Sigma$ ground state with the following magnetic parameters in solid neon (assuming $g_\parallel = 2.002$): $g_\perp = 1.999(1)$, $|D| = -0.0107(1)$ cm^{-1}, $|A_\parallel(\mathrm{Mn})| = 490(5)$, $|A_\perp(\mathrm{Mn})| = 418(1)$, $|A_\perp(\mathrm{F})| = 60(1)$, and $|A_\parallel(\mathrm{F})| = 85(2)$ MHz. MnF is then highly ionic with the spin density on each F^- probably less than about 5%. The Mn^+ ion exhibits about 60% of the s character of the free ion. MnF_2 is linear with a $^6\Sigma_g$ ground state with magnetic parameters in solid neon (assuming $g_\parallel = 2.002$): $g_\perp = 1.994(5)$, $|D| = 0.370(3)$ cm^{-1}, $|A_\parallel(\mathrm{Mn})| = 153(6)$, $|A_\perp(\mathrm{Mn})| = 124(1)$, $|A_\perp(\mathrm{F})| = 19(1)$ MHz. Comparison of these parameters is made with those obtained earlier from crystalline MnF_2 and similar magnetic crystals.

Proc. Symp. on High Temperature Metal Halide Chemistry (Edited by D.L. Hildenbrand and D.D. Cubicciotti) Proceedings Vol. 78-1 pages 187-198 (The Electrochem. Soc. Inc., 1978).

AN INVESTIGATION OF THE FIRST ROW TRANSITION-METAL FLUORIDE MOLECULES USING ESR SPECTROSCOPY

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ABSTRACT

The ground state electronic configuration and magnetic parameters have been determined for several first row transition metal mono-, di-, and tri-fluoride molecules from their ESR spectra at 4°K. The molecules studied have high spin electronic configurations with less than 5% of the free electron spin density residing on the fluorine(s), indicative of highly ionic bonding. Theory and experiment have been correlated to establish or predict their ground electronic states and geometries.

High spin molecules: ESR and optical spectroscopy of MnH ($^7\Sigma$) and MnH_2 ($^6A_1$) at 4°K[a]

R. J. Van Zee, T. C. DeVore,[b] J. L. Wilkerson,[c] and W. Weltner, Jr.

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(Received 6 April 1978)

MnH and MnH_2 molecules, and their deuterated counterparts, have been trapped in argon and neon matrices at 4°K and observed via infrared, visible, and electron-spin-resonance spectroscopy. The data for MnH support the gas-phase $^7\Sigma$ ground-state assignment and yield the magnetic parameters $|A(\mathrm{H})| < 20$, $A_\parallel(\mathrm{Mn}) = 322(6)$, $A_\perp(\mathrm{Mn}) = 299(2)$ MHz, $g_\perp = 2.001(1)$ (assuming $g_\parallel = g_e$), $D = -0.002(1)$ cm^{-1}. The derived MO description is in essential agreement with the *ab initio* calculations of Bagus and Schaefer. Infrared data indicate that MnH_2 is bent at a bond angle of 117 ± 30°, and stretching force constants are derived. ESR spectra variations with the matrix used and with isotopic substitution indicate motional effects in some matrices. It is concluded that the ground state is $^6A_1$ with $|D| = 0.20(2)$ cm^{-1} and with the probable hyperfine parameters $|A(\mathrm{H})| = 36$, $A_{xy}(\mathrm{Mn}) = 73$ MHz, where xy is an average axis perpendicular to the H-H direction. The bent molecule is justified by Walsh-type theory applied to transition-metal dihydrides. There are indications that the MnH_3 molecule may have also been observed.

THE ASTROPHYSICAL JOURNAL, 231:632–636, 1979 July 15

THE FeH MOLECULE AT 4 K

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Received 1978 November 9; accepted 1979 February 5

ABSTRACT

FeH and FeD molecules have been trapped in solid argon at 4 K. From the observed infrared frequencies, corrected for small solid-state effects, the gas-phase vibrational properties are predicted to be $\omega_e'' = 1764\,(10)$ and $\omega_e x_e'' = 46\,(5)\,\mathrm{cm}^{-1}$. D_0 is found to be 2.0 eV from the Birge-Sponer approximation, but is more likely near 1.7 eV on the basis of the application of that approximation to other diatomic hydrides. Five weak electronic transitions (suggesting low gf values) observed in absorption in the 4000–5000 Å region are probably counterparts of the blue and green band systems in the gas-phase laboratory and stellar spectra. The strongest band occurs at 4190 Å, suggesting that the 4288 Å band studied by Heimer be reinvestigated. Failure to observe an ESR spectrum of FeH in the solid is interpreted as support for an orbitally degenerate ground electronic state, in agreement with the theoretically derived $^6\Delta$ ground state.

Subject headings: molecular processes — transition probabilities

CrH and CrH_2 molecules: ESR and optical spectroscopy at 4°K

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(Received 20 March 1979; accepted 24 May 1979)

CrH and CrD molecules have been trapped in solid argon at 4°K. Infrared spectra, when the large anharmonicity is accounted for, yield predicted gas phase vibrational parameters in the ground state $\omega_e = 1615\ \mathrm{cm}^{-1}$ and $\omega_e x_e = 17\ \mathrm{cm}^{-1}$. ESR spectra clearly establish that the molecule has a $^6\Sigma$ ground state with zero-field-splitting $|D| = 0.34(1)\ \mathrm{cm}^{-1}$ in solid argon and approximate hyperfine coupling constants $|A(H)| = 49(5)$ MHz, $|A_\perp(^{53}Cr)| = 53(5)$ MHz, and $g_\parallel \approx g_\perp = g_e$. Several "extra lines" (off-principal-axis absorptions) in the ESR support the assignment. CrH_2 (and CrD_2, CrHD) was observed in the IR spectra and may also have been detected in the ESR, which tentatively suggest a $S = 2$ molecule with $|D| \cong 0.02\ \mathrm{cm}^{-1}$.

National Bureau of Standards Special Publication 561, Proceedings of the 10th Materials Research Symposium on Characterization of High Temperature Vapors and Gases held at NBS, Gaithersburg, Maryland, September 18-22, 1978. Issued October 1979.

TRANSITION-METAL MOLECULES AND WALSH'S RULES--RATIONALIZATION OF OPTICAL AND ESR DATA

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The electronic and molecular structures of the transition-metal difluoride, dioxide, and dihydride molecules are rationalized or predicted from proposed molecular orbitals and Walsh-type diagrams based upon optical and ESR spectroscopic data.

ESR of matrix isolated bromine atoms produced in the $H+Br_2$ reaction [a)]

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(Received 31 October 1979; accepted 1 May 1980)

The products of the H(D) + X_2 reaction, where X is Br, Cl, or F, have been trapped in solid argon at 4 °K and observed via ESR. With Br_2 as reactant the observed spectra are attributed to Br atoms electronically quenched in an axial crystal field. The spectra obtained using the other halogens were not clearly attributable to quenched atoms. The ESR of matrix-isolated Br atoms has not been observed previously. [While this paper was being reviewed, H. Muto and L. D. Kispert observed the ESR spectrum of partially quenched Br atoms in x-irradiated N-bromosuccinimide single crystals [J. Chem. Phys. **72**, 2300 (1980)]] but their magnetic properties are similar to those recently observed by Iwasaki, Toriyama, and Muto for I atoms quenched in solid xenon. For Br: $g = 2.646(1)$, $g = 1.55(1)$, $|A| = 1937(20)$ MHz, $|A| = 423(10)$ MHz, and $Q = 100(10)$ MHz. Comparison was made with crude axial crystal field predictions derived using the magnetic parameters of the gas-phase atoms.